DRAFT RSET WHITE PAPER #4 – Evaluation of Modern Pesticides in Sediments

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QUESTION/ISSUE: Are modern pesticides (e.g., organophosphorus, carbamates, triazines, etc.) accumulating in sediments at potentially toxic levels? Should certain modern pesticides be listed as "chemicals of special occurrence" to be considered for evaluation in areas affected by agricultural runoff?

DISCUSSION: The persistence of modern pesticides, and their ability to accumulate in sediments at potentially toxic levels, is not well studied. Sediment sampling for modern pesticides in areas affected by agricultural runoff is rare; recent sediment sampling of the Lower Snake River by the USACE Walla Walla District has shown common detections of only one modern pesticide, linuron, a phenyl urea compound. This White Paper provides a review of agricultural usage rates, environmental occurrence, and chemical properties which may be used to prioritize modern pesticides on a project-specific basis for further evaluation. Because no sediment quality guidelines are available for these chemicals, they would be classified as "chemicals of special occurrence", and would be analyzed during agency investigations or monitoring programs and where there is a "reason to believe" they are present, primarily in areas affected by agricultural runoff. After sufficient data have been collected (including synoptic chemistry and bioassay data), these chemicals may be evaluated to determine whether they contribute to sediment toxicity, and if so, whether the observed effects are predictable enough to support the development of screening levels.

The modern pesticides database is compiled in Table 1. This table contains chemical properties, usage data, environmental occurrence, and other parameters which are used to help prioritize the need for further study of these chemicals.

Chemicals of Interest:
Based on research conducted by the US Geological Survey (USGS, 1997; 2002) in Willamette and Yakima Valleys, the following types of pesticides are in common use in the Pacific Northwest:

- Organophosphorus
- Carbamates
- Thiocarbamates
- Phenyl Urea
- Triazine Compounds
- Others

Methods of Analysis:
Numerous methods are available for analysis of modern pesticides. Because of the diversity of types of modern pesticides, no one method provides comprehensive coverage. Also, certain pesticides may be analyzed by customization of existing EPA methods (e.g. 8081 or 8270), whereas others are not clearly associated with any EPA method.

Approximate costs and practical quantitation limits (PQLs) for commercial analysis of sediment by the various pesticide methods is provided below:

- EPA 8081 (OC Pests): $160 [PQL ~ 1 to 5 ppb]
- EPA 8141 (OP Pests): $190 [PQL ~ 10 to 50 ppb]
- EPA 8151 (OC Herbicides): $200 [PQL ~ 10 to 50 ppb]
- EPA 8270 (Semivolatiles): $400 [PQL ~ 50 to 100 ppb]
- EPA 8318 (Carbamates): $170 [PQL ~ 100 ppb]
- EPA 8321 (Phenyl Urea): $250 [PQL ~ 25 ppb]

Although each analysis alone is not particularly expensive, to run all possible pesticide methods could run well over $1,000. The Walla Walla district has successfully analyzed a fairly broad suite of pesticides (organochlorine, organophosphorus, and organonitrogen) using a customized 8270 analysis. This may have some application as a fairly inexpensive reconnaissance method, since 8270 analysis is already required for many sediment characterization projects to quantify PAHs, phenols, and other organic compounds. However, there may be some loss of sensitivity with 8270 compared to other methods such as 8141.

Evaluation Criteria:
Pesticide evaluation criteria are summarized in Table 1 and described briefly below.

Agricultural Application Rates. Application rates (pounds applied per year to the Yakima or Willamette basin study areas) have been estimated by the USGS. Because the climate, crop types, and cropping practices are different on the east and west sides of the Cascades, the two areas are characterized by different pesticide usage rates and preferences.

Detection in River Water. Detection frequencies of modern pesticides in rivers and streams in the Willamette and Yakima basins are summarized in Table 1. Water quality statistics (50^{th} and 90^{th} percentiles, and maximum concentrations) are also presented. Similar to the geographic differences in pesticide usage, the river waters in the eastern and western study areas are characterized by different suites of detected pesticides.

Detection in River Sediment. Some of the most comprehensive studies of modern pesticides in Pacific Northwest sediments have been performed by the USACE Walla Walla District (2003). At sites on the Lower Snake River and near the Clearwater River confluence, linuron was the only modern pesticide detected, at concentrations ranging from 28 to 77 ug/kg. Using equilibrium partitioning theory, based on an interim Environment Canada (1999) aquatic life criterion of 7 ug/L, and an average sediment organic carbon content of 2 percent, an estimated sediment screening value for linuron is 210 ug/kg. Thus, the observed linuron concentrations do not appear to be high enough to cause adverse biological effects.

Exceedence of Water Quality Criteria. EPA water quality criteria are only available for some organophosphorus pesticides (EPA, 2002). Water quality criteria for certain other

modern pesticides have been developed by Environment Canada (2002). A thorough review of the basis and applicability of the Canadian values is beyond the scope of this paper. The maximum detected concentrations for a few pesticides exceeded their aquatic life criteria; however in all but one instance, the 90th percentile concentrations did not exceed the criteria. The one exception is azinphos-methyl (guthion), an organophosphorus pesticide; in the Yakima basin, the 50th and 90th percentile concentrations of this pesticide exceeded the EPA chronic criterion. Aside from this one constituent in Yakima, this evaluation suggests occasional water quality excursions are possible, probably close to the area of application, but exceedences are not ubiquitous or routine, and are likely short-lived.

Hydrophobicity. The organic-carbon partitioning coefficient (K_{oc}) is a measure of the hydrophobicity of modern pesticides. Log K_{oc} values are low to moderately low, ranging from 1.24 to 3.63. By comparison, the log K_{oc} value for DDE is about 100 to 10,000 times higher (5.44). In general, modern pesticides are not strongly hydrophobic, and will exhibit a weak tendency to adsorb to sediments.

Environmental Persistence. Environmental persistence is expressed in terms of half life, based primarily on empirical lab or field experiments (SRC, 2004). The half lives of modern pesticides are relatively short, ranging from a few days or a few months, to a maximum of about 1.5 years. By comparison, the half life of DDE is about 10 to 100 times longer—15 to 25 years. Based on these data, modern pesticides will degrade relatively quickly in the environment, through biodegradation, hydrolysis, and other processes.

REFERENCES:

Environment Canada, 2002, Canadian Environmental Quality Guidelines. http://www.ccme.ca/assets/pdf/e1_06.pdf

Syracuse Research Corporation, Environmental Fate Database CHEMFATE and BIODEG. Sponsored by EPA and maintained by Dr. Philip Howard. http://www.syrres.com/esc/efdb.htm

U.S. EPA, 2002, National Recommended Water Quality Criteria, Office of Water, Office of Science and Technology, EPA-822-R-02-047.

U.S. Geological Survey, 1997, Distribution of dissolved pesticides and other water quality constituents in small streams, and their relation to land use in the Willamette River Basin, Oregon, 1996. Prepared by C.W. Anderson, T.M. Wood, and J.L. Morace, Water-Resources Investigations Report 97-4268, Portland, OR.

U.S. Geological Survey, 2002, Pesticides in surface water of the Yakima River Basin, Washington, 1999-2000—their occurrence and an assessment of factors affecting concentrations and loads. Prepared by J.C. Ebbert and S.S. Embrey, Water-Resources Investigations Report 01-4211, Portland, OR.

RECOMMENDATION: Modern pesticides appear to pose a relatively low risk of sediment toxicity, but may deserve further study in areas dominated by agricultural land use and runoff. In general, modern pesticides are short lived in the environment and exhibit a weak tendency to adsorb to sediments. In river and stream samples, exceedences of water quality criteria are uncommon. Sediment samples collected by the Walla Walla district to date have detected only linuron, at concentrations below those likely to cause adverse effects.

Organophosphorus pesticides have the highest ranking for further evaluation, because: (1) these chemicals are in common use in both Willamette and Yakima basins; (2) these chemicals have somewhat higher partitioning coefficients (2.67 to 3.63) compared to many other modern pesticides; (3) these chemicals have some of the more stringent aquatic life criteria, and the only domestic (i.e., EPA derived) aquatic life criteria; (4) azinphos-methyl (guthion) was the one pesticide that exceeded aquatic life criteria in a large percentage of samples from the Yakima basin. Triazine compounds are a secondary priority for study, because these are among the compounds most frequently detected in agricultural river water on both sides of the Cascades. Organophosphorus and triazine compounds may be analyzed using either EPA Method 8141 or a customized Method 8270. Method 8141 is recommended because it appears to provide better sensitivity.

The need to analyze other types of modern pesticides may be determined on a case-by-case basis. For example, the Walla Walla District may continue to monitor linuron in sediments of the Lower Snake River, based on detections in previous sampling events.

PROPOSED LANGUAGE:

8.4.2. Chemicals of Special Occurrence.

<Add the following paragraph:>

Organophosphorus Pesticides. Testing for organophosphorus-based and potentially other types of modern pesticides (e.g., triazines) may be required in areas dominated by agricultural land use and in sediments affected by agricultural runoff. Analysis by EPA Method 8141 is recommended.

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